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Near-infrared quantum cutting in Ho^{3+}/Yb^{3+} co-doped $BaZr_{0.8}Y_{0.2}O_{3-\delta}$

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ABSTRACT

A novel $Ho^{3+} \rightarrow Yb^{3+} \rightarrow Ho^{3+}$ multi-step energy transfer caused quantum cutting under 455 nm excitation is observed in Ho^{3+}/Yb^{3+} co-doped $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ phosphor. During the quantum cutting process, Yb^{3+} ions efficiently increase the particle population of $^5I_6$ level of Ho^{3+}, resulting in 10 and 8 times of enhancement of Ho^{3+} emission at 1216 nm ($^5I_6 \rightarrow {}^5I_8$) and 1926 nm ($^5I_7 \rightarrow {}^5I_8$), respectively. It is interesting that the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ emission of Yb^{3+} ions themselves is very weak although the quantum cutting is performed by the Ho^{3+}/Yb^{3+} ion-pairs. The result indicates that the $Yb^{3+} \rightarrow Ho^{3+}$ back energy transfer in the $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ phosphor is quite efficient and helpful for the enhancement of Ho^{3+} emission in near infrared region. A new valid method based on luminescence intensity ratio is developed to estimate the quantum cutting efficiency. It is found that the energy transfer form Ho^{3+} to Yb^{3+} is 52.8% in the phosphor with optimum Ho^{3+}/Yb^{3+} doping concentration and 90% of near infrared emission of Ho^{3+} is performed by the multi-step energy transfer induced quantum cutting.

1. Introduction

Luminescent materials with quantum efficiency (QE) higher than unity have attracted great interests for their potential application in the fields of plasma displays, mercury-free fluorescent lamps, solar cells and so on [1]. In recent decades, rare-earth-doped materials with near-infrared down-conversion (DC) quantum cutting (QC) luminescence have attracted great attention for their potential applications in photovoltaic solar cells or photo-detectors based on crystalline Si [2–7]. Many Ln^{3+}/Yb^{3+} couples such as Tm^{3+}/Yb^{3+} [8], Pr^{3+}/Yb^{3+} [6], Tb^{3+}/Yb^{3+} [2] , Er^{3+}/Yb^{3+} [4] and Nd^{3+}/Yb^{3+} [3] that can convert near ultraviolet or visible photons into near-infrared photons have been witnessed.

According to the properties of the energy-transfer process, the DC QC performed by Ln^{3+}/Yb^{3+} pairs can be divided into two types: one is first-order DC and the other is second-order DC [9]. First-order DC is a cross relaxation process occurring between couples of matched energy levels, while second-order DC is a process during which a sensitized ion at high level transfers its energy to two other luminous ions at a lower energy level. It is believed that first-order QC may have a higher probability than the second-order one. However, efficient DC using Yb^{3+} via resonant energy transfer requires donor ions with an energy level at about 20 000 cm^{-1} and an intermediate energy level at approximately 10 000 cm^{-1}. Consequently efficient first-order DC can be expected only for the couples Pr^{3+}/Yb^{3+}, Nd^{3+}/Yb^{3+}, Er^{3+}/Yb^{3+} and Ho^{3+}/Yb^{3+} [9]. Among these Ln^{3+}/Yb^{3+} couples, Ho^{3+}/Yb^{3+} couple is a good choice in NIR QC investigation because of the favorable metastable energy levels of Ho^{3+} ion and considerable energy match between Yb^{3+} and Ho^{3+}. Moreover, Ho^{3+}/Yb^{3+} couple is capable to convert both near UV and visible light into near infrared emission due the level structure of Ho^{3+}. Recently NIR QC in Ho^{3+}/Yb^{3+}-co-doped materials such as Y_2O_3:Yb^{3+}/Ho^{3+} [10] and β-$NaYF_4$:Ho^{3+}/Yb^{3+} [11] has been reported. Nevertheless, the QC properties of Ho^{3+}/Yb^{3+} couple in different hosts are still worth exploring.

Over the past decade, rare earth doped ABO_3-like oxide with perovskite structure have been reported possessing very interesting luminescent properties. The ABO_3-like oxides have in the A-site a divalent alkaline earth element, such as Ba, Sr and Ca, and in the B-site a tetravalent element (Ce, Zr, Ti) [12,13]. The perovskite-type oxides phosphors are very stable and can steadily work in various environments [14]. Moreover, perovskite-type oxides phosphors have been found to be potential candidate in field emission display (FED) and plasma display panel (PDP) devices because they are sufficiently conductive to release electric charges stored on the phosphor particle surfaces [15]. Thus a great deal of perovskite-type oxide phosphors activated by rare earth ions, including Ce^{3+}, Sm^{3+}, Tm^{3+}, Pr^{3+}, Eu^{3+}, Tb^{3+} and so forth [16–21], have been prepared and their luminescent properties were investigated. On the other hand, the studies on up-conversion of Yb^{3+}/Tm^{3+} [22] and Yb^{3+}/Er^{3+} [23] co-doped perovskite-type oxide phosphors have also been reported. However, there are few reports on DC emission of rare earth ions in perovskite-type oxides.

$BaZrO_3$, doped with rare earth ions, is one of widely investigated perovskite-type phosphors [22,23]. In ordinary $BaZrO_3$ host, doped trivalent rare earth ions tend to substitute octahedral Zr^{4+} sites

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[24,25]. The electric dipole f–f transitions of trivalent rare earth ions are strictly forbidden in a regular octahedral field according to the selection rule. Fortunately, the ZrO_6-octahedron is usually distorted in $BaZrO_3$ matrix. Meanwhile, the substitution of Zr^{4+} sites by trivalent rare earth ions will result in O^{2-} vacancies due to the charge imbalance between Zr^{4+} and Ln^{3+} ions. The two factors alter the local symmetry around the doped trivalent rare earth ions and make the f–f transition of trivalent rare earth possible. It is reported that 1/5 of Zr^{4+} ions can be replaced by Y^{3+} in $BaZrO_3$, forming a $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ oxide without changing the basic structure [26–29]. In the $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ oxide, the heavily doped Y^{3+} ions and a large amount of O^{2-}vacancies caused by Y^{3+} doping might effectively adjust the local symmetry around the rare earth ions. Thus increased the f–f transition of the doped trivalent rare earth is in accordance with expectation.

Herein, in the present work, we prepared Ho^{3+}/Yb^{3+} co-doped $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ oxides with perovskite structure that have been synthesized by co-precipitation method. The crystalline structures, NIR QC luminescence properties of phosphors with different concentrations of Ho^{3+} and Yb^{3+} ions, are studied and the QC mechanism in Ho^{3+}/Yb^{3+} co-doped $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ phosphors is discussed in detail.

2. Experimental

Co-precipitation technique is a good method for preparation of luminescent material with relatively high melting point, which can make the raw material refining and homogeneous mixing, lower the calcinations temperature and reduce the calcinations time. Therefore, in our experiment, the $BaZr_{0.8-x}Y_{0.2-y}O_{3-\delta}$: xHo^{3+}, yYb^{3+}(x = 0.01, 0.02, 0.05, 0.1, 0.15, 0.2; y = 0, 0.01, 0.02, 0.05, 0.08, 0.12, 0.15, 0.18, 0.2) samples were prepared by the co-precipitation synthesis procedure. Zirconium oxychloride octahydrate ($ZrOCl_2{\cdot}8H_2O$), barium chloride dehydrate ($BaCl_2{\cdot}2H_2O$), Yttrium oxide (Y_2O_3), Ytterbium oxide (Yb_2O_3), Holmium oxide (Ho_2O_3), nitric acid (HNO_3) and ammonium hydroxide ($NH_3{\cdot}H_2O$) were used as the starting materials. All the reagents were of the analytical purity. A procedure for the sample synthesis of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$: Yb^{3+}-Ho^{3+} is typically described as follows: firstly, Y_2O_3, Yb_2O_3 and Ho_2O_3 were dissolved in dilute nitric acid under condition of stirring and heating, respectively. After the Y_2O_3, Yb_2O_3 and Ho_2O_3 were completely dissolved, the excess nitrite acid was removed at high temperature. Then a certain amount of de-ionized water was added to obtain $Y(NO_3)_3$, $Yb(NO_3)_3$ and $Ho(NO_3)_3$ solution with concentration of 1 mol/L. $ZrOCl_2{\cdot}8H_2O$ and $BaCl_2{\cdot}2H_2O$ were also dissolved in de-ionized water to obtain the solution with concentration of 1 mol/L and 0.1 mol/L, respectively. Subsequently, these solutions were mixed with proper ratio according to the designed target product, and stirred for 0.5 h to obtain a new homogeneous solution. Then the white precipitate was formed by slowly dropping $NH_3{\cdot}H_2O$ with magnetic stirring. The precipitate was filtrated and washed four times with de-ionized water, and then twice with ethyl alcohol, and followed by drying at 120°C for 24 h. In the end, the precipitate was pre-sintering at 550 °C for 3 h to obtain the white powder. The powder was grinded and annealed at 1100 °C for 3 h in air to obtain the white phosphor sample.

The structure of the samples was identified by X-ray diffraction (XRD) on a Bruker D8 advance equipment using Cu tube with Kα radiation of 0.15406 nm in the 2θ range of 20° to 80°. The emission spectra were obtained by a monochromator (Zolix Instrument, Omni-λ320i) coupled with photomultiplier (PMTH-S1-CR131) and NIR sensitive detector (DInGaAs 2600-TE). Diode lasers at 455 nm and 980 nm were used as excitation sources in the measurement. The luminescence decay curves were measured by a FLS920 (Edinburgh) spectrometer. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns of the $BaZr_{0.8-x}Y_{0.2-y}O_{3-\delta}$: xHo^{3+}, yYb^{3+}(x = 0.05, 0.1, 0.2; y = 0, 0.05, 0.12, 0.15, 0.2) powders. The diffraction peaks of the XRD pattern of $BaZr_{0.8-x}Y_{0.2-y}O_{3-\delta}$: xHo^{3+}, yYb^{3+} are consistent with that of standard powder diffraction of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ [30,31], indicating that all of the $BaZr_{0.8}$-$xY_{0.2}$-$yO_{3-\delta}$: xHo^{3+}, yYb^{3+} compounds were successfully synthesized with the co-precipitation method. The prepared $BaZr_{0.8-x}Y_{0.2-y}O_{3-\delta}$: xHo^{3+}, yYb^{3+} compounds also have cubic perovskite-structure belonging to the Pm-3m space group. It is believed that in $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ host Y^{3+} (Yb^{3+}, Ho^{3+}) ions usually occupied Zr^{4+} sites [21,32].

The luminescence spectra in NIR region of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ doped with various concentrations of Ho^{3+} ions (fixed Yb^{3+} concentration at 12%) on the 455 nm excitation are shown in Fig. 2. NIR PL peaked at 1216 nm (Ho^{3+}:$^5I_6 \rightarrow {}^5I_8$) and 1926 nm ($Ho^{3+}$: $^5I_7 \rightarrow {}^5I_8$) were observed for all the samples. The relationship of 1216 nm and 1926 nm intensities tendency with Ho^{3+} ions concentrations are also given in the inset of Fig. 2. It is found that the integrated intensities of the NIR emission bands centered at 1216 nm and 1926 nm increase firstly and then decrease with the increasing concentration of Ho^{3+}, respectively. Both 1216 nm and 1926 nm emissions reach their maximum intensities when the Ho^{3+} concentration is 10%. With Ho^{3+} concentration increasing, more Ho^{3+} ions in the phosphor can absorb the excitation light and the energy transfer (ET) from Ho^{3+} to Yb^{3+} ion and back energy transfer (BET) from Yb^{3+} to Ho^{3+} ions also become more efficient due to the shortened distance between the Yb^{3+} and Ho^{3+} ions. As a result, the near infrared emission intensities increase as Ho^{3+} concentration increases. However, the 1216 nm and 1926 nm emission intensities tend to decrease with further increasing the Ho^{3+} ion concentration owing to the concentration quenching effect.

After the optimum doping concentration Ho^{3+} is confirmed, the Yb^{3+} concentration dependent near infrared emission is further investigated. Fig. 3 shows visible-NIR emission luminescence spectra of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ doped with various concentrations of Yb^{3+} ions (fixed Ho^{3+} concentration at 10%) under 455 nm excitation. In the inset of Fig. 3a, the integrated intensity of the NIR emission band centered at 1216 nm and 1926 nm also become stronger with increasing Yb^{3+}

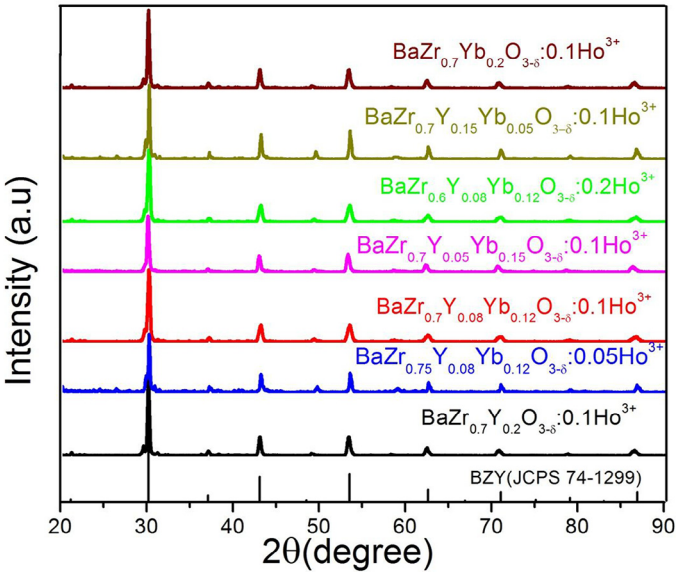

Fig. 1. Powder X-ray diffraction patterns of the $BaZr_{0.8-x}Y_{0.2-y}O_{3-\delta}$: xHo^{3+}, yYb^{3+} (x = 0.05, 0.1, 0.2; y = 0, 0.05, 0.12, 0.15, 0.2) powders.